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Subtractively Normalized Interfacial Fourier Transform
Infrared Spectroscopy of Difluorobenzene Adsorbed at
Polycrystalline Platinum Electrodes

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SUBTRACTIVELY NORMALIZED INTERFACIAL FOURIER TRANSFORM

INFRARED SPECTROSCOPY OF DIFLUOROBENZENE ADSORBED

AT POLYCRYSTALLINE PLATINUM ELECTRODES

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ABSTRACT

The subtractively normalized interfacial Fourier transform infrared spectra (SNIFTIRS) of the difluorobenzenes in perchloric acid solutions show that the species are absorbed flat at low concentrations of the substrate. In concentrated solutions, the packing changes to a skewed configuration. For these molecules there is no indication of vibrational coupling to the strong electrical field at the electrode surface and the vibrational spectra are as predicted by the standard surface selection rule.

INTRODUCTION

The study of adsorption of organic molecules at electrode surfaces is important to the areas of heterogeneous catalysis, corrosion, battery and fuel cell development, and electrosynthetic applications, to name a few. Conventional electrochemical methods can provide a great deal of information about surface excesses of adsorbed species and strength of bonding of adsorbates at these surfaces. Recent work by Hubbard et al has shown that it is possible to infer the molecular orientation of adsorbed organic species at platinum electrodes using an elegant differential thin layer technique (1). These workers have subsequently provided information regarding the effects on the molecular orientation as a function of concentration of subtrate (1), temperature (2), and electrolyte properties (3). These current-based methods cannot provide answers to questions concerning the detailed nature of surface bonding or the structural perturbation of the molecule due to its interaction with that surface. The information provided, however, is invaluable in the design of spectroscopic experiments and can lead to increased confidence in their interpretation.

Information regarding the vibrational structure of adsorbed species can now be obtained using the in situ techniques of surface enhanced Raman spectroscopy (SERS (4)), surface unenhanced Raman spectroscopy (SUERS (5)), electromodulated infrared spectroscopy (EMIRS (6-8)), and subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS (8-10)). At this time, although it is theoretically possible, useful and unambiguous data regarding orientation of adsorbed species at metal electrodes has not been possible utilizing the two former methods. For the infrared techniques, however, the pattern of relative intensities for the various normal mode vibrations of the adsorbed molecule can be directly related to its

orientation by using the surface selection rule. We recognize that there will
be difficulties in certain cases due to intensity changes arising from
structural perturbation of the adsorbed molecule, and from several types of
vibronic coupling with the high electric field at the interface (including the
Stark Effect) (7, 8, 11). In this paper, we report data which demonstrates
the utility of SNIFTIRS in determining the orientation of the difluorobenzenes
at polycrystalline smooth platinum surfaces.

<center>EXPERIMENTAL</center>

CHEMICALS

The fluorobenzenes were obtained from Aldrich and were distilled from a
0.5 m Vigreaux column before use. Collection was made over argon. The
support electrolyte was 1.0 M perchloric acid (Matheson Reagent) which was
prepared by dilution of the 70% commercial product. Water used was obtained
from a Barnstead deionization apparatus, which was subsequently distilled
twice from a quartz apparatus. The fluorobenzenes were delivered to the acid
solution flasks by means of a gas-tight syringe. Concentrations were
calculated by difference weighing of the syringe. The fluorobenzenes were
dissolved in the solvent/electrolyte by agitation with a magnetic stirrer for
at least one hour.

CELLS AND ELECTRODES

The cell utilized was of the conventional SNIFTIRS specular reflectance
type (9) (Figure 1). The optical window was intrinsic silicon, and was in the
shape of a 50 mm disk 1.0 mm in thickness. The cell was fitted with gas inlet
and outlet ports for degassing the solution during the measurement operation
when required. The reference electrode was saturated calomel, and was
isolated from the main cell by a compartment with a wetted stopcock and a
Luggin capillary probe placed 2 mm from the face of the working electrode.
The secondary electrode was a platinum ring which was placed in the cell so
that the working electrode fitted through the center of the ring. The ring
was about 1 cm from the face of the working electrode. The working electrode
itself was a platinum disk mirror mounted on the end of a brass shaft. The
diameter of the disk and shaft were 7 mm, and they were encased finally in a
sheath of 9 mm O.D. Kel-F fluorocarbon. The platinum disk face was polished

by using sucessively finer grades of alumina, ending with a final treatment of 0.03 micron diameter particles. The use of a fine grained balsa wood polishing block helps prevent the imbedding of alumina particles into the metal, since they are effectively retained by the balsa.

The electrode was brought as close as possible to the optical window to reduce the pathlength through the solution (9). The cell was then mounted in the sample cavity of the spectrometer in a retroreflection apparatus (described previously (9)).

INSTRUMENTATION

The electrochemistry was driven by a Hi-Tek waveform generator and potentiostat (Models PPR1 and DT2101 respectively). A Digilab Qualimatic spectrometer, hardware modified to coadd subsequent interferograms, was used to obtain the spectra. The modification involved the inverting of alternate interferograms acquired by the instrument by a fast analog inverter. The data-acquire trigger from the spectrometer was used to switch the electrode potential via the potentiostat system between two values. Thus the alternate interferograms, at different potentials, were automatically subtracted by the spectrometer instead of being added. The stored interferogram was thus a difference interferogram of the two potential states, and could be transformed in the normal manner. The use of this method for acquiring the data was effective in the reduction of instrument drift, and in impressive exclusion of spectral interferences from residual atmospheric water vapor and carbon dioxide. It should be pointed out at this point that most of the smaller utility FTIR spectrometers do not allow the convenient coadding and switch/coadding software enhancements necessary to perform effective high sensitivity surface measurements. In many cases, however, this disadvantage,

which may be overcome by simple personal computer interfacing or slight hardware changes, is offset by sometimes highly desirable features such as the great energy throughput of the Qualimatic.

The spectra in this work were obtained at 4 wavenumber resolution nominally.

RESULTS AND DISCUSSION

Thirteen of the normal vibrational modes of p-difluorobenzene are infrared active. These are listed in Table 1 along with their description and assigned frequencies. These bands were obtained from conventional difference solution spectra made in the electrolyte solution. Assignments were listed after comparison with literature values. All of these modes represent dipole changes in the plane of the aromatic ring except for the last three. The surface selection rules for vibrational spectroscopy at metal interfaces require that for a transition to be allowed, there must be a component of the change in the dipole derivative with respect to the normal coordinate perpendicular to the surface where the species is constrained. In addition, the transition can be induced only by radiation which has an electromagnetic field component perpendicular to the interface (p-component) (8). The s-component of the electromagnetic field at a conductor interface will suffer a complete phase change upon reflection, which results in a vector cancellation of the field strength at the surface. Hence radiation which is polarized parallel to the surface (perpendicular to the reflection plane) cannot induce infrared transitions in adsorbed dipoles at conducting interfaces. The SNIFTIRS spectrum for the p-difluorobenzene species is then quite easy to predict in terms of this surface selection model. The b_{3u} modes, each with dipole derivative changes perpendicular to the molecular plane, will be expected to undergo absorption of radiation if the species is adsorbed with the molecular plane parallel to the metal surface ("flat" adsorption). The b_{1u} and b_{2u} modes would not be expected to absorb radiation since their dipole changes all lie in the molecular plane. The converse is true for adsorption of the species with the molecular plane perpendicular to the metal surface ("edge" adsorption). For any intermediate position ("skew" adsorption) all

transitions will be expected.

The SNIFTIRS spectrum for p-difluorobenzene (0.5 mM in 1.0M perchloric acid) between the potential limits of 0.200V (base potential) and 0.400 V vs NHE at a platinum mirror electrode is shown in Figure 2. The bands extending to positive values of $\Delta R/R$ correspond to absorption by the predominant species in the optical path at +0.200 V, the solution dissolved p-difluorobenzene. The bands extending to negative values correspond to the adsorbed species at +0.400 V. It should be pointed out that the total quantity of p-difluoro-benzene in the thin layer of solution between the electrode and the optical window is less than that required to form a complete flatly adsorbed monolayer of difluorobenzene. Any solution dissolved p-difluorobenzene that may be present in the thin layer at the higher potential will manifest itself as a decrease in the magnitude of the positive extending bands. It is observed that there are no negative bands corresponding to the b_{1u} and b_{2u} modes. There are, however, two new bands corresponding to two of the b_{3u} modes normally occurring at 833 and 509 cm^{-1}. Under the present conditions these are shifted to 811 and 495 cm^{-1} respectively. These results strongly suggest that the molecular species is adsorbed on the platinum metal surface in a flat configuration. The red shift in the b_{3u} modes in the adsorbed state is expected since interaction of the surface with the π-electrons of the aromatic system will tend to decrease the bond orders involved in those modes.

The SNIFTIRS spectra of the meta- and ortho- isomers are shown in Figure 3. These show again that the molecule lies flatly adsorbed at the more positive potential. Negative bands are observed that are associated with each of the normal vibration absorptions which have dipole derivative changes perpendicular to the principal molecular symmetry plane. In no instance is there a corresponding band for adsortion for the fundamentals which are

associated with in-plane vibrational modes.

Figure 4 shows the results of an experiment where the potential modulation amplitude is varied. The absorption band pictured corresponds to the b_{3u} C-C-C out-of-plane bending mode. As the potential is increased from the same initial base of 0.200 V to more positive potentials, the negative band corresponding to the adsorbed species is seen to undergo an increasingly larger red shift, in accord with the comments mentioned above. Any such shift with potential is attributed to adsorbed species only. It is noted that the positive band of the solution dissolved species is unaffected by the change in potential as expected. The integrated area under the positive and negative lobes are equal to within experimental accuracy, and it is thought that there is approximately monolayer coverage (9). It is also important to note that even at the highest potential used there is no sign of bands from the b_{1u} and b_{2u} modes. Although, as explained earlier, these are disallowed by the surface relection rule, they could appear by a mechanism which is essentially a manifestation of the Stark Effect and involves vibronic coupling to the high electrical field at the electrode surface (7, 8, 11). We conclude, therefore, that for the fluorobenzenes the polarizability changes during the b_{1u} and b_{2u} vibrations are too small to lead to observable field effects.

Hubbard and Soriaga (1) have made similar observations for a number of adsorbates in the same electrode/electrolyte system. One paper of their series points to the restructuring of the adsorbed layer when the isotherm equilibrium is shifted strongly to the surface by increasing the concentration of the solution dissolved species. The results for an experiment involving the effect of substrate concentration is shown in Figure 5. The potential modulation was from 0.200 to 0.400 V. Again, the electrolyte was perchloric acid, and the spectrum represents the b_{3u} C-C-C bending mode. The temperature

of the cell was 281K. Up to concentrations of about 0.5mM, the entire spectrum is identical to that described above. At solution concentrations above 0.8 mM however, there is a marked increase in the magnitude of the bands and negative bands now appear for all of the modes instead of just the b_{3u} species. We attribute the appearance of these new bands, and the increase in intensity to an increase in surface density of adsorbed species by the forced edgewise packing by virtue of the increased solution concentration (1). The b_{1u} and b_{2u} modes are now able to interact with the radiation since the skewed species will have perpendicular dipole derivative components for every fundamental mode.

It is clear that it is possible to observe not only the vibrational spectra and thus the energetics of adsorbed species, but also make some deductions regarding surface orientation. With the increased senstivity of instruments designed specifically for surface studies, both SNIFTERS and EMIRS, it should be possible in the near future to record spectra of species that are adsorbed at very low coverage levels, as well as spectra of very short lived intermediates at metal catalytic surfaces. It is necessary not only to be able to record these spectra, but also to be able to determine which surface species are primarily responsible for the formation of the observed products, and which are neutral or passivating to the catalysis.

ACKNOWLEDGEMENTS

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FIGURE LEGENDS

Figure 1.   The spectroelectrochemical cell used in the SNIFTIRS experiment.

Figure 2.   Difference spectrum for p-difluorobenzene at a platinum mirror
             electrode in 1.0 M perchloric acid solution. Modulation limits
             are +0.200 V vs. NHE (base potential) and +0.400 V. (a) and (b)
             1600 normalized scans, (c) and (d) 450 normalized scans.

Figure 3.   Difference spectra (450 normalized scans) for m- and o-
             difluorobenzene under conditions as described in Figure 2.

Figure 4.   Difference spectrum (690 normalized scans) of p-difluorobenzene
             as a function of the magnitude of the modulation potential.
             Other parameters are the same as those in Figure 2.

Figure 5.   Difference spectrum (690 normalized scans) of p-difluorobenzene
             as a function of substrate concentration. Other parameters are
             the same as those in Figure 2.

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